THE EISENHOWER LIBRARY
3 1151 02676 0235

195.57

Library

of the
Johns Hopkins University

A STUDY OF THE VAPOR PRESSURE OF AQUEOUS SOLUTIONS

OF CANE SUGAR AT

TWENTY DEGREES

BY

HUGH KIMMEL BAKER

DISSERTATION

Submitted to the

Board of University Studies of the Johns Hopkins University

in conformity with the requirements for the

Degree of Doctor of Philosophy

Baltimore 1901

175,657

TABLE OF CONTENTS

ABSTRACT

INTRODUCTION 1

EXPERIMENTAL 1

Apparatus 3

Procedure 4

Data 10

Summary of Experimental Data 31

DISCUSSION OF RESULTS

Deviation from Raoult's Law 33

Deviation from van't Hoff's Law 26

Osmotic Pressure and Vapor Pressure Lowering 31

Osmotic Pressures of Concentrated Solutions Calculated by Porter's Equation 33

Osmotic Pressures of Concentrated Solutions Calculated by Lewis' Equation 35

Calculated Osmotic Pressures of Dilute Solutions 37

Summary of Calculated and Observed Osmotic Pressures 40

SUMMARY 41

BIBLIOGRAPHY

ACKNOWLEDGMENT

The author desires to express his appreciation of the assistance, encouragement and inspiration given by Professors Frazer and Lovelace under whose direction this research was carried out.

To them, as well as to Professors Reid, Patrick, Morley and Dr. Thornton, the writer wishes to acknowledge a debt of gratitude for instruction in the lecture room and laboratory.

THE VAPOR PRESSURE LOWERING OF AQUEOUS CANE SUGAR SOLUTIONS AT 20°.

INTRODUCTION.

The study of the vapor pressures of aqueous solutions of cane sugar offers an excellent opportunity for the correlation of colligative properties, especially so in the case of osmotic pressures since in both lines investigations can be carried out over a comparable wide range of concentrations. The accurate vapor pressure measurements at the present time of Frazer and Lovelace but limited to temperature, it seems possible that they may also be extended over the temperature range covered by osmotic pressure. There is also the possibility of the experimental verification of the thermodynamic relation between osmotic pressure and vapor pressure lowering. Osmotic pressures calculated by the thermodynamic relations of the colligative properties are in quite good agreement with the experimental data of the direct measurements by Morse,[1] Frazer[2] and co-workers and Berkeley, Hartley and co-workers.[3]

The vapor pressures of the cane sugar solutions are not so numerous and have been measured in most cases by the dynamic method. Berkeley, Hartley and Burton[4] measured the

1 Am. Chem. Journal 46 263, (1911)
2 J. Am. Chem. Soc. 33 1116, (1911)
3 A. 376 (1907)
4 A. 309 177 (1908)

lowerings at 0° and claim an accuracy of 1% by their method. Washburn,[1] using a modified form of the apparatus of Berkley and Hartley, was able to obtain the values for a weight molar concentration at 25° which agreed well with the observed osmotic pressure values of Morse.

One of the first to observe vapor pressures of aqueous solutions by a static method using a Rayleigh manometer was Smits,[2] who worked with $NaNO_3$ and NaCl solutions. Wood[3] has measured the vapor pressures of concentrated sugar solutions at high temperatures by a static method. The static method has some decided advantages over the dynamic methods, which will not be enumerated at this time, except in regard to the fact that the general equation of Porter[4] is derived on just such conditions as are encountered in the static method, namely; the solution is under the hydrostatic pressure of its own vapor.

Wood's method of static determination is limited to concentrated solutions and high temperatures where large differences of pressure occur, but for the precision necessary for the measurement at lower temperatures and concentrations, the static method of Frazer and Lovelace[5] is well adapted. The fact that the vapor pressure of the solution is compared directly with

1 J. Am. Chem. Soc. 31 897 (1915)
2 Zeit phy Chem 91 34 (1904)
3 Chem. News 113 91 (1916)
4 Proc Roy Soc A 79 519 (1907)
5 J.Am.Chem.Soc. 34 1662 (1914) Zeit phy Chem 89 100

that of the pure solvent under exactly similar conditions and that the setting and reading error is within 0.0005 mm actual lowering, leave little doubt as to the superiority of the method. Moreover, careful studies of the removal of dissolved air from the solutions by Rogers[1] and Beese[2] have eliminated that source of error.

Measurements have been made on mannite[3] by this method, and because of the fact that sugar shows all the properties of a hydrated non-electrolyte, and has been carefully investigated by various methods, including osmotic pressure, it seemed desirable to be able to compare the respective vapor pressure lowerings, as well as the osmotic pressures. For these reasons, and to be able to compare the osmotic pressures calculated by Porter's equation from statically determined vapor pressures with the direct measurements, sugar was chosen as the solute.

Apparatus.

The apparatus which had been standing idle for a period of about four years was thoroughly overhauled, cleaned with nitric acid and cleaning mixture, and finally steamed to remove any acid fumes that might remain. The mercury was

1 J.Am.Chem.Soc. 43 1795 (1921)
2 ibid 43 102 (1921)
3 loc. cit.

redistilled and that required for the Rayleigh gauge, the McLeod gauge and the thermoregulator was specially treated according to the method of Hulett.[1] During the war the Gaede pump which was originally used, had been removed and was replaced by a Langmuir mercury condensation pump in series with a General Electric auxiliary pump of large capacity. Between the auxiliary pump and the condensation pump was situated a small manometer, a stop cock to cut off between the two pumps, and a stop cock connected by a "T" in the line to a capillary for the purpose of relieving the vacuum either on the system or the Langmuir pump after closing trap #1. A phosphorus pentoxide bulb was connected by a "T" and a ground glass joint in the glass just above the condensation pump to prevent water vapor being drawn into the oil of the auxiliary pump. With these exceptions the system used was that described by Lovelace, Frazer and Sease.[2]

Experimental Procedure.

The sugar used was from the same source as that used in the osmotic pressure work here in this laboratory. It was not recrystallized, but showed a negligible amount of reducing sugar when tested with Fehling's solution (Allihn's method).

1 Phy. Rev. 33 307
2 loc cit

Comparative analyses between it and sample furnished by the Bureau of Standards on the saccharimeter and the interferometer revealed a presence of about .04% impurity in the solute used.

Bureau of Standards #17 sugar analysis.

Moisture	less than	0.05%
Ash	" "	.002%
Reducing substances estimated as invert sugar	less than	.02%

In the preparation of solutions in vacuo, the same technique was followed as described by Sease and Rogers[1] in the case of dilute solutions. However in the preparation of concentrated solutions, because of the great bulk of the sugar required, it was necessary to place the sugar in the larger bulb. The air was removed from the water in the small bulb by boiling cautiously with a smoky flame and sealing the constriction after about 30 minutes. The bulb containing the sugar was evacuated with the Langmuir pump for about an hour at the end of which time the McLeod gauge showed negligible air pressure. The bulb was then sealed at the constriction. The bulbs containing air free sugar and air free water were joined at the stems by a short rubber tube from which the air had been displaced by distilled water and the latter by cream

1 loc cit

mercury, and which were wired into position by a double ligature at each end. The tips, which had been filed [illegible] before making the joint, were broken within the rubber connection and when the sugar and all dissolved the "introduction" bulb was completely filled with solution. By closing the rubber connection with a screw clamp, the larger bulb could be removed without exposing the solution to the air and the introduction of filling fitted in its place.

It was feared that the sugar might invert during the time required for the removal of air and the measurement of the vapor pressure, and thus increase the number of solute particles. Careful tests were made and it was found that in one case no inversion had occured over a period of 32 days. These tests were made by comparing the concentrations of the solutions as introduced against the concentrations found out by the interferometer and by the Z concentrometer.

Table 1.

0.1M Stood [illegible] days

$\frac{[illegible]^{\circ}}{34.44^{\circ}} = \frac{\text{Removed}}{\text{Introduced}} =$ [illegible] by saccharimeter

$\frac{.09[illegible]}{.0[illegible]} = \frac{\text{Removed}}{\text{Introduced}} =$ [illegible] by interferometer

0.2M Stood 20 days

$\frac{50.197^{\circ}}{50.31} = \frac{\text{Removed}}{\text{Introduced}} = 1.0037$ by saccharimeter

$\frac{.1992}{.1985} = \frac{\text{Removed}}{\text{Introduced}} =$ [illegible] by interferometer

0.7M Stood 5 days

$\frac{75.475^{\circ}}{76.00^{\circ}} = \frac{\text{Removed}}{\text{Introduced}} =$ [illegible] by saccharimeter

$\frac{.695[illegible]}{.67305[illegible]} = \frac{\text{Removed}}{\text{Introduced}} =$ [illegible] by interferometer

3.0M Stood 7 days

$\frac{[illegible]^{\circ}}{[illegible]} = \frac{\text{Removed}}{\text{Introduced}} =$ [illegible] by saccharimeter

$\frac{[illegible]}{[illegible]} = \frac{\text{Removed}}{\text{Introduced}} =$ [illegible] by interferometer

The above ratios show that within the error of the saccharimeter reading except in the case of the 0.1M [illegible] one would [illegible] enough to conclude that little or no inversion occurred.

The [illegible] in determining when the solutions were air free as used by the other observers working on this method, were adopted and confirmed.

The analysis of the solutions was made by the interferometer after calibrating its sensitivity at the various concentrations. The known solutions were carefully made up and the weighings corrected to vacuo. A little difficulty was encountered in reading the bands of the interferometer at the higher concentrations, due to the fact that they were more or less distorted and straighten only on long standing, which might involve some loss by evaporation. With some practice it was found that the readings could be taken satisfactorily after allowing 30 minutes for temperature differences to equalize, even tho the bands were not straight.

EXPERIMENTAL DATA.

0.0960 Roller Readings

Date	Zero Before	Reading	Zero After	Deflection
3/25/21	196.0	241.3	196.3	
	196.0	241.2	196.0	
	196.1	241.3	196.3	45.20
	195.8	240.7	195.5	
	195.3	240.8	195.6	
	195.3	240.8		45.20
3/2/21	195.7	240.9	196.0	
	196.0	241.0	196.0	
	196.0	241.1		
	196.0			45.04
	195.7	241.0	195.9	
	195.7	241.2	195.9	
	195.7	241.0		45.26

Mean of average deflection 45.17

0.0011 Meter Readings

Date	Zero Before	Readings	Zero After	Deflection
3/11/21	195.7	255.0	196.0	
	196.0	255.1	196.0	
	196.0	255.0		
	196.0			59.07
	195.7	254.7	195.9	
	195.7	254.6	195.9	
	195.7	254.7		58.88
3/22/21	196.0	255.0	196.0	
	196.0	255.0	196.0	
	196.1	255.0	196.0	58.97
	195.6	254.5	195.5	
	195.6	254.6	195.6	
	195.6	254.6		58.99

With readings of 3/22/21 Average 58.93

S.Hill Point Readings

Date	Zero Before	Reading	Zero After	Deflection
1/21/21	249.05	274.06	250.06	25.00
1/21/21	249.13	274.10	249.13	24.97
1/21/21	249.93	275.00	250.03	25.02
1/24/21	249.11	274.13	249.16	25.02
1/31/21	247.86	272.98	247.96	25.12

Mean of average deflections 25.06

0.9937 Molar Readings

Date	Zero Before	Reading	Zero After	Deflection
1/27/21	248.15	314.23	248.12	66.09
"	248.06	314.00	248.03	65.94
1/24/21	249.93	315.00	249.96	65.94
"	249.13	315.03	249.13	65.90
2/1/21	247.17	313.03	247.10	65.90
"	247.13	313.06	247.13	65.93
		Mean of average deflections		65.93

0.0991 Molar Readings

Date	Average Zero Before & After	Reading	Deflection
12/29/20	248.2	254.10	5.90
12/30/20	247.5	253.8	6.30
12/30/20	247.7	253.9	6.20
		Mean of average	6.13

N.B. These readings were chosen as best values because the average zeros before and after the reading checked within 0.1 mm and both observers check.

Other readings on this concentration were discarded because of the inexperience of the observers and because zeros before and after, and readings themselves, did not check within 0.1mm.

0.1992 Molar Readings

Date	Average Zero Before & After	Reading	Deflection
12/30/20	247.3	259.7	12.40
12/30/20	247.6	259.8	12.20
	Mean of average deflections		12.30

Note: These readings were chosen as best values because the average zeros before and after the reading checked within 0.1 mm.

Other readings on this concentration were discarded because of the inexperience of the observers and because either the zeros before and after or the readings themselves did not check within 0.1 mm.

2.0162 Molar Readings

Date	Zero Before	Reading	Zero After	Deflection
3/1/21	246.4	392.1	246.5	
	246.4	392.0	246.5	
	246.2	392.1	246.4	145.70
	245.3	390.9	245.2	
	245.3	391.0	245.3	
	245.3	391.0		145.69
2/27/21	246.1	392.1	246.2	
	246.3	392.1	246.2	
	246.3	392.0		145.81
	246.2	392.0	246.5	
	246.3	392.3	246.2	
	246.5	392.2	246.3	
	246.4			145.84

With Readings on 2/26/21 Mean or average Reflections 145.89

2.9916 Mole Readings

Date	Zero Before	Reading	Zero After	Deflection
3/12/21	194.7	426.4	194.8	
	194.6	426.4	194.9	
	194.7	426.2	195.0	231.53
	194.0	425.9	194.2	
	194.2	425.9	194.1	
	194.0	425.9		231.8 ?
3/10/21	194.7	426.1	194.7	
	194.8	426.3	194.8	
		426.1	194.8	231.47
	194.0	425.4	194.0	
	194.0	425.5	194.9	
	194.0	425.4	194.0	231.47
		Mean of Average deflections		231.49

Equation reading because temperature of bath dropped .01 of a degree.

4.0063 Molar Reading

(Read against 2.0162M)

Date	I 4M Reading	II 2M Reading	III Average Zero	Deflection
2/27/21	430.33	393.05	246.21	
	430.03	392.18	246.34	
3/1/21	431.03	393.90	246.28	
	429.86	391.50	246.61	
	430.03	392.06	246.56	
	429.46	390.96	246.69	
3/26/21	430.73	393.26	247.21	
	430.03	393.30	247.18	
		Average 2M deflection		146.09
		Average 2M vs 4M deflection		100.72
		4 Molar deflection		345.61

I.E. The 4 Molar deflection is obtained by subtracting the average of column III from the average of column I and adding this difference to that obtained by subtracting the average of column III from the average of column II. Maximum reading error 0.4, deviation from the mean.

4.3615 Noise Readings
(Read against L.9916)

Date	I 5M Reading	II 3M Reading	III Average Zero	Deflection
3/10/41	386.96	426.16	194.69	
	386.03	425.13	193.96	
3/12/41	386.95	426.30	194.80	
	386.10	425.90	194.01	?
		Average 5M		231.49
		Average 5M vs 3M		192.16
		5M Deflection		423.65

Question reading because temperature of bath dropped .01 of a degree.

Method of determination of 5M deflection is the same as described for the 4M.

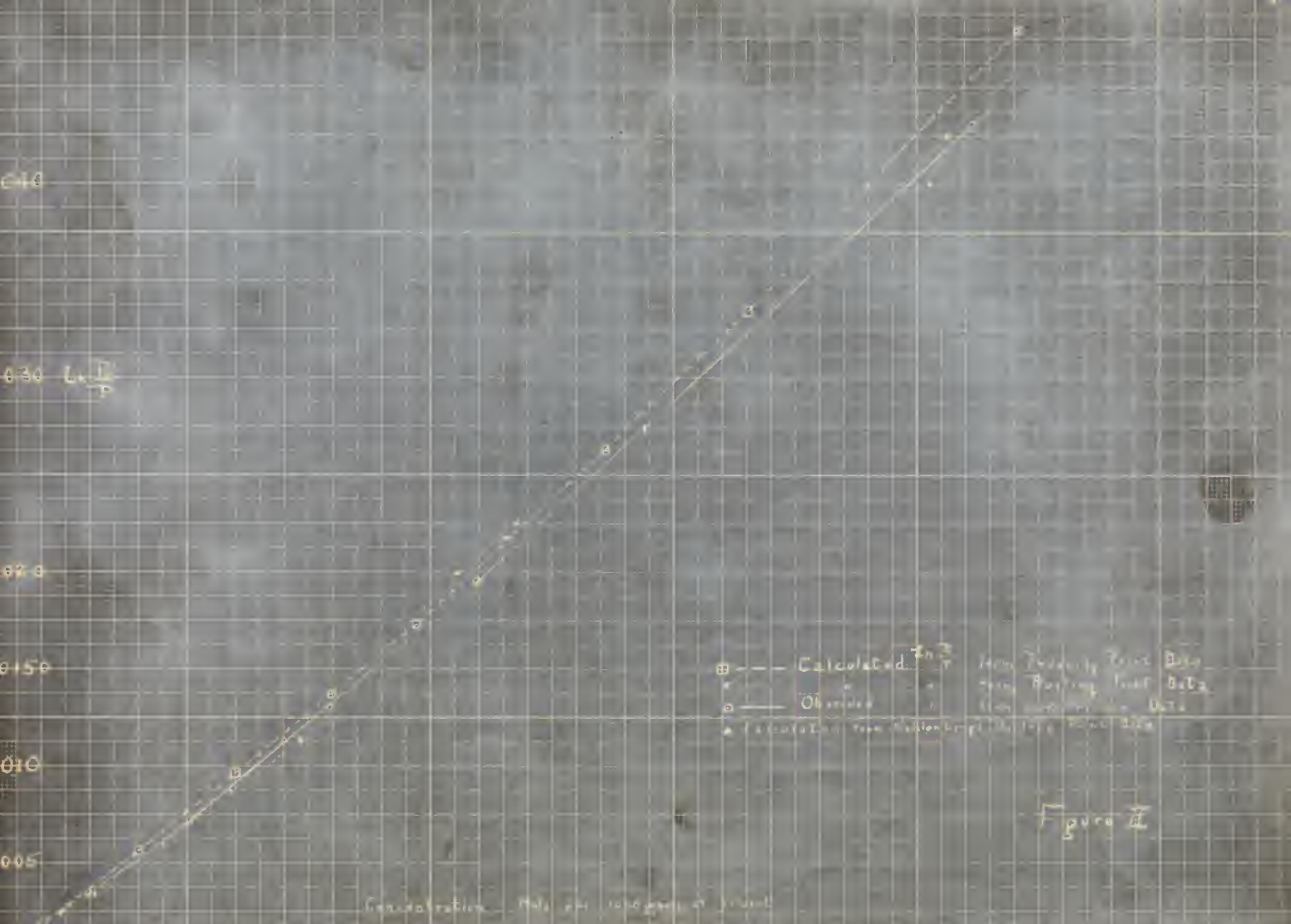
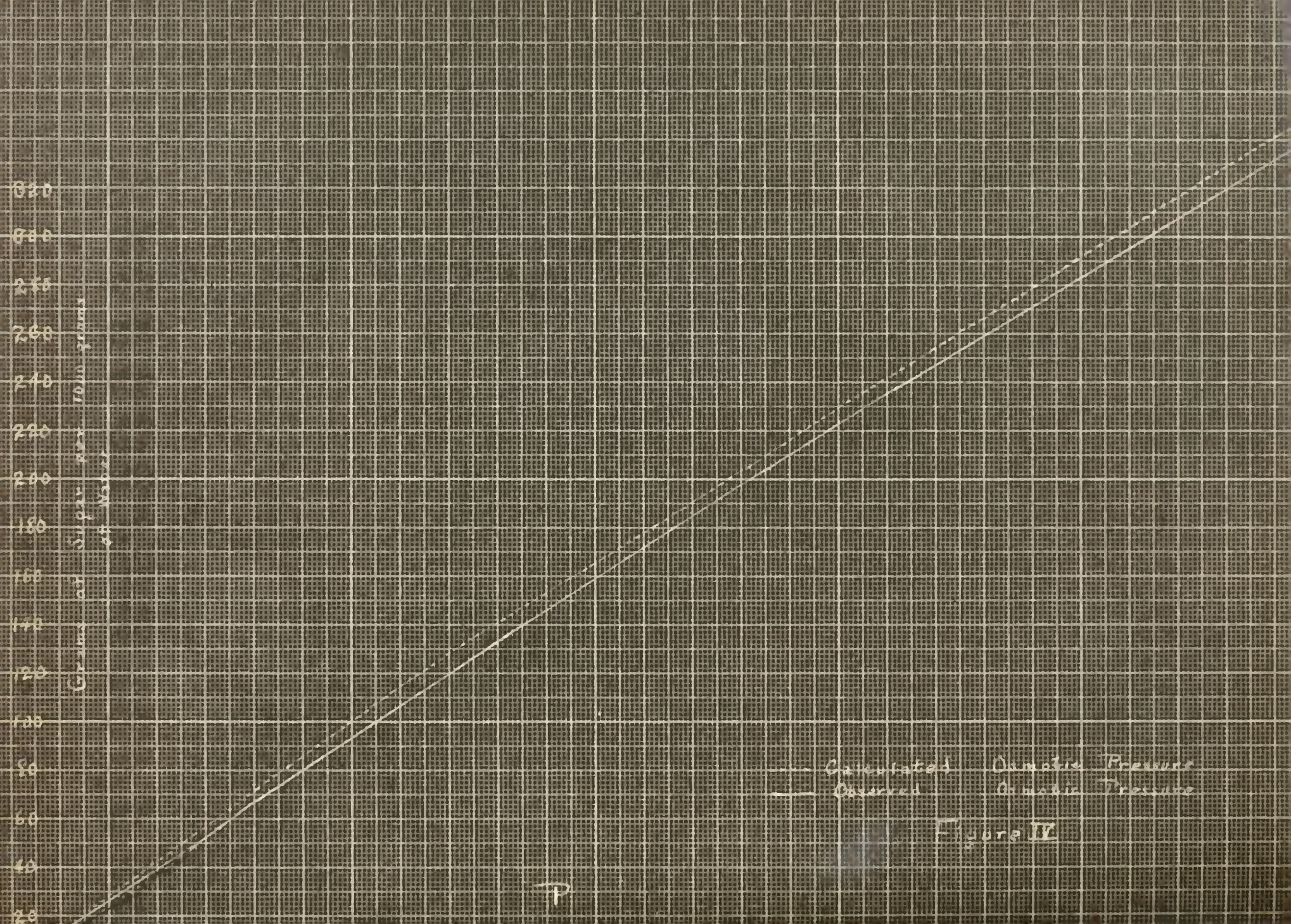


Figure 4


Saturated Osmotic Pressure
Observed Osmotic Pressure
Figure IV
P

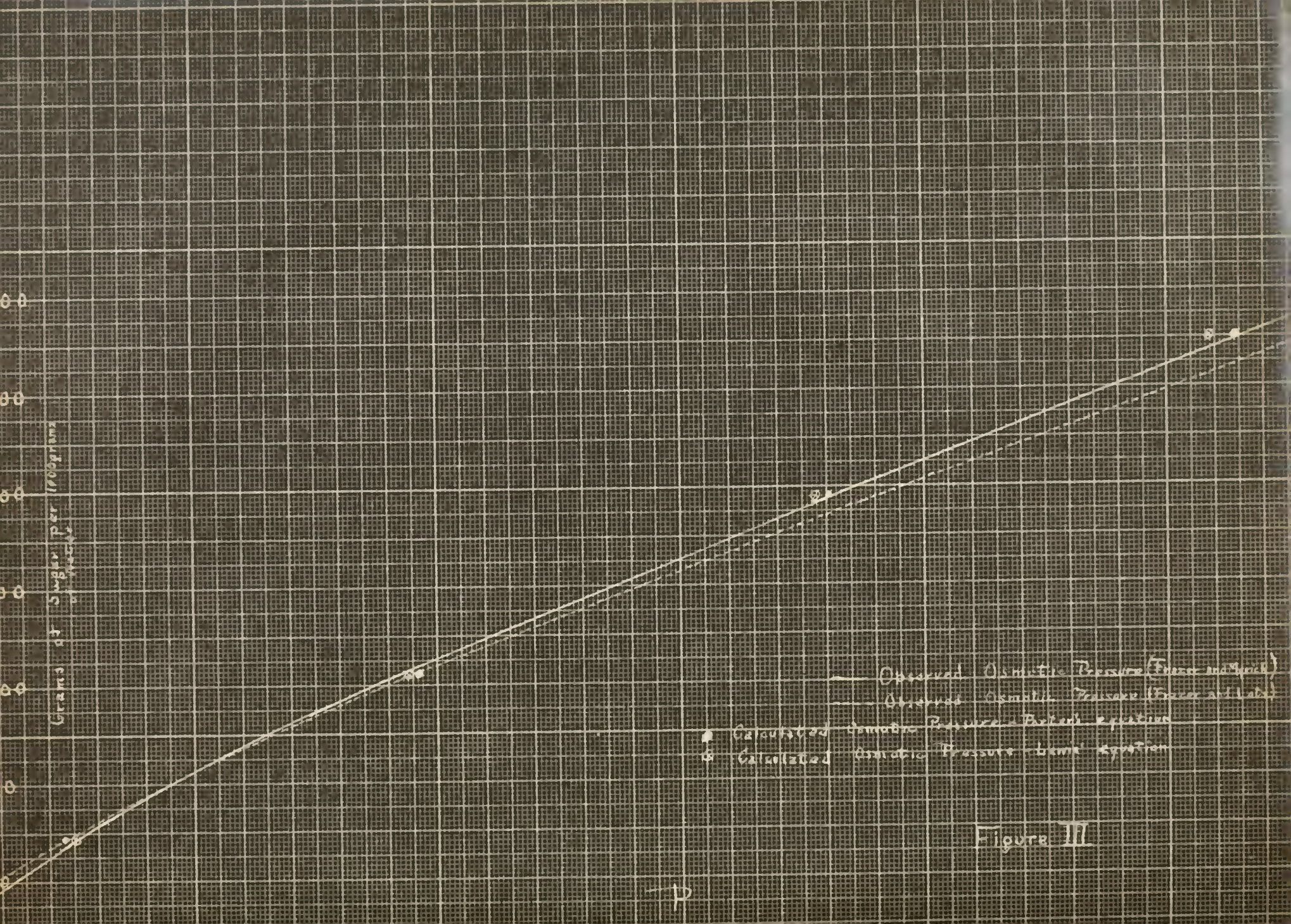

Grams of Sugar Per 100 grams Water
Observed Osmotic Pressure (Force method)
Observed Osmotic Pressure (Beans method)
Calculated Osmotic Pressure Berkeley equation
Calculated Osmotic Pressure Lewis equation
P

Figure II

Table 11.

SUMMARY OF DATA.

G = Grams of sugar per 1000 grams of H_2O (in vacuo)

M = Molar concentration

s = Deflection

k = Constant used in determination of lowering $\frac{d}{D} \cdot \frac{\sin\theta}{\frac{1}{2}\tan 2\theta}$

P_o-P=Lowering at room temperature 25°

h = Lowering corrected to 0°

G	M	s	$k \times 10^{-6}$	P_o-P	h
58.39	0.0991	6.13	3094	0.0312	0.0311
63.13	0.1992	12.30	3094	0.0627	0.0625
127.17	0.4011	25.03	3094	0.1273	0.1270
200.37	0.6011	38.35	3094	0.1954	0.1949
287.37	0.8980	53.17	3094	0.2701	0.2694
388.34	1.1934	68.95	3122	0.3570	0.3563
489.54	1.4916	115.39	3094	0.7452	0.7393
1025.13	1.9916	251.49	3069	1.1734	1.1661
1366.39	1.9986	144.39	3094	0.7452	
		183.78	3085	0.9539	1.9394
1703.37	1.9913	221.49	3061	1.1734	
		192.16	3074	0.9750	2.1387

Table III.

Deviations from Raoult's Law.

M = Molar concentration

h = Lowering corrected to 0^{o}

Calc. = Lowering calculated from Raoult's Law

$\frac{P_o - p}{M}$ = Molecular lowering

M	h	Calc	Diff.	Mol Fraction $x10^{-4}$	$\frac{P_o - p}{n/N+n}$	$\frac{P_o - p}{M}$
0.0991	0.0311	0.0312	0.0001	17.8	17.466	0.3137
0.1992	0.0623	0.0627	0.0004	35.7	17.470	0.3151
0.4011	0.1270	0.1257	0.0013	71.6	17.740	0.3166
0.6011	0.1975	0.1977	0.0098	107.0	18.459	0.3285
0.8060	0.2291	0.2170	0.0121	125.7	18.622	0.3291
0.8137	0.3365	0.3082	0.0281	175.7	19.142	0.3584
2.0162	0.7098	0.8148	0.1256	350.2	21.124	0.3669
2.9916	1.1081	0.9118	0.2563	519.8	22.476	0.3904
3.0368	1.0804	1.1881	0.4813	677.5	24.547	0.4158
4.0715	1.4397	1.4133	0.0264	833.8	25.995	0.4298

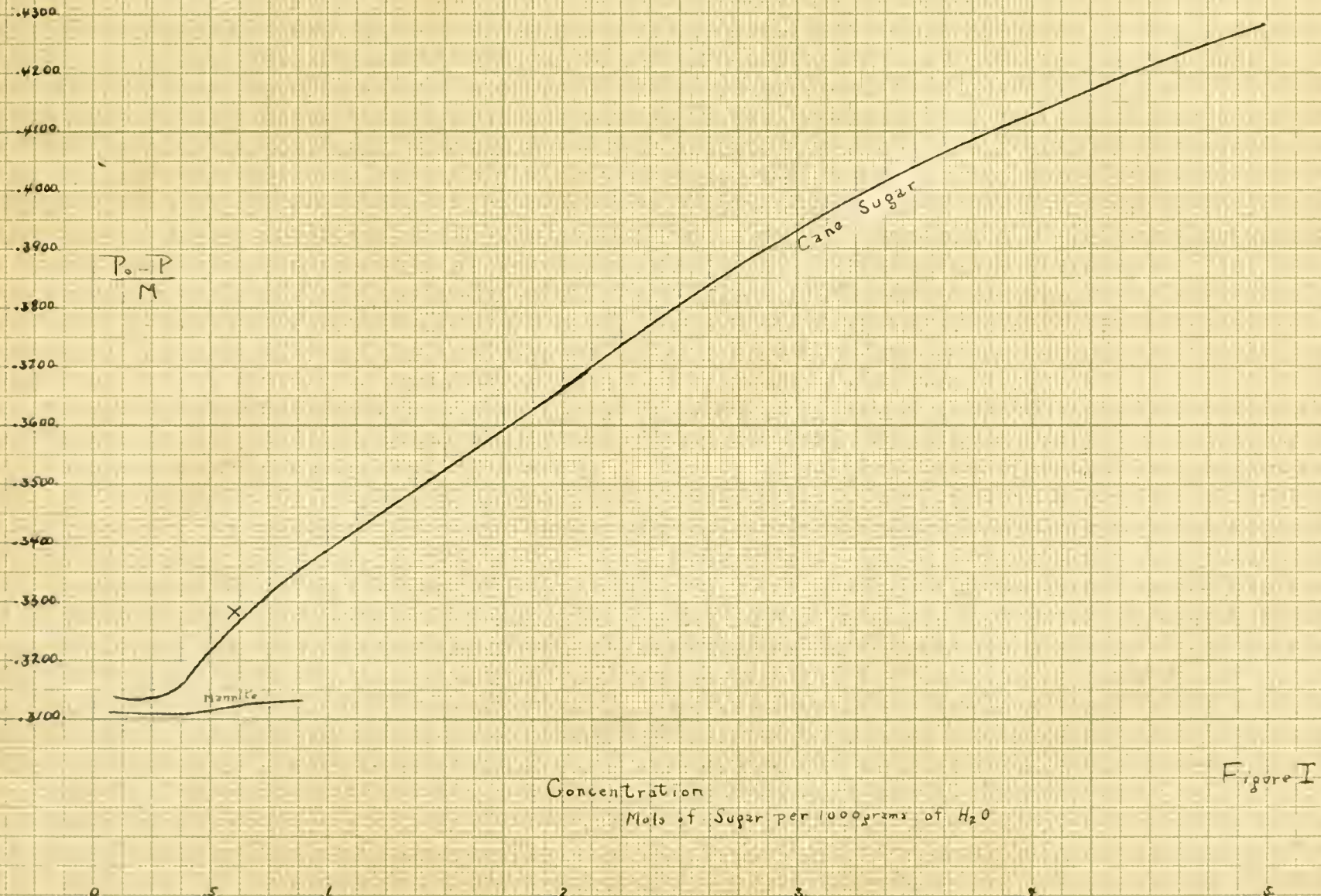

.4300
.4200
.4100
.4000
.3900
.3800
.3700
.3600
.3500
.3400
.3300
.3200
.3100
$\frac{P_o - P}{M}$
Cane Sugar
Mannite
Concentration
Mols of Sugar per 1000 grams of H_2O
0
.5
1
2
3
4
5

Figure I

Discussion of Results

Deviation of Sugar Solutions from Raoult's Law.

The results tabulated in Table III show a marked divergence from the theoretical lowerings required by Raoult's law.

$$\frac{P_0 - P}{P_0} = \frac{n}{N+n} \quad \text{or} \quad P = P_0 \frac{N}{n+N}$$

The differences between the calculated and observed values are recorded under the heading "Diff." and are expressed in millimeters of mercury. By plotting the values of the molecular lowering $\frac{P_0 - P}{n}$ against concentration of both sugar and mannite, it can be seen how the slope of the sugar curve, Figure 1, differs from the mannite. Because of the limited solubility of the mannite this curve must be extrapolated beyond one molar for comparison between a substance that obeys Raoult's law and one that does not. The theoretical molecular lowering curve is a straight line parallel to the concentration axis. The column of Table II headed, lowering divided by the mol fraction, shows the calculated value for the vapor pressure of the pure solvent at 20° to the increase over the actual constant value which is 17.5 mm of mercury according to Scheel & Heuse.

These abnormalities of vapor pressure lowering and other colligative properties of sugar solutions are usually

explained by assuming that the solute forms hydrates in solution, or in other words, some of the water is held back in chemical combination with the sugar. Various investigators have calculated the amount of hydration of sugar. Callendar[1] obtains a value of five molecules of water combined with one molecule of sugar based on the boiling point determinations of Hanlemberg.[2] Washburn[3] calculates from the freezing point data that sugar exists in solution as a hexahydrate. Findlay[4] states, assuming water is not associated, and that the pressure of the solute has not altered the association of water, that the osmotic pressure calculated assuming sugar to be a hexahydrate is in almost exact agreement with Morse's[5] observed value at 20° for a weight molar solution. Wood[6] calculates from static vapor pressure lowerings that sugar is a tetrahydrate at the higher temperatures and concentrations. Frazer & Myrick[7] say that the degree of hydration varies with concentration and pressure and on the assumption that water

1 Proc Roy Soc A 80 466 (1908)
2 J Physical Chem 5 362 (1901)
3 Technological Quarterly (Proc.) 21 360 (1908)
4 "Osmotic pressure" monograph p42
5 loc cit
6 loc cit
7 loc cit

is in the dihydrol form they obtain a tetrahydrate for 5M concentration by their osmotic pressure data at 30°. At 3, 5 and 4 molar concentrations they calculate that the pentahydrate exists.

Results calculated from the data of this research seem to indicate that sugar is a tetrahydrate in solution altho they do not show the presence of a definite hydrate. Table IV is calculated from Raoult's law and assumes no association of the solvent.

Table IV.

n = Mols of Sugar per 1000 grams H_2O (55.555 mols)

N = Mols of Water calculated to represent active water (water with escaping tendency)

H = Mols of Water calculated to be in combination with 1 mol of sugar at that particular concentration.

n	N	H
0.0991	55.800	
0.1992	55.738	
0.4011	54.881	1.68
0.6011	52.651	4.70
0.6960	52.437	4.41
0.9567	51.058	4.45
2.0162	45.693	4.89
2.9918	41.592	4.67
4.0368	38.249	4.29
4.9015	35.617	4.00

The degree of combination between sugar and water is difficult to determine because of the fact that water is known to be associated, and the effect of the presence of a solute on association and especially the effect of the presence of a hydrated solute is not known. An interesting parallel phenomonon is observed in that simultaneously with the retaining of active water by the sugar, there is a diminution of volume in the preparation of solutions. A solution of cane sugar in water does not occupy as large a volume as would be expected from molecular volume considerations. In other words the solution is made up of components that are not truly additive. Bousfield and Lowry and Richards postulate that the more voluminous constituent of the ternary mixture of water has been removed or has been acted upon as the case may be. If there is hydrate formation the active water is partially changed into hydrate water, the volume changes and the vapor pressure, which is the measure of active water, relatively diminishes, and thus it seems that the shrinkage of volume on dissolution substantiates the theory of hydrates of sugar in solution.

0.040
0.030
Ln $\frac{P_o}{P}$
.020
.0150
.010
.005
Concentration Mols per 1000 grams of Solvent
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
Calculated $\ln \frac{P_o}{P}$ from Freezing Point Data
" " from Boiling Point Data
Observed " from Vapor Pressure Data
Calculated from Kahlenbergs Boiling Point Data

Figure II

Deviation from Van't Hoff's Law

The temperature coefficient of vapor pressure of sugar solutions is of interest since it affords a means of comparison with the observed osmotic pressure temperature coefficient. Van't Hoff's law states that the relative vapor pressure lowerings are independent of the temperature, that is, $\frac{\partial}{\partial T}\left(\ln \frac{p}{p_0}\right) = 0$. It is obvious from Figure 11 that such conditions do not exist for sugar solutions, even tho in the absence of vapor pressure measurements at other temperatures it was necessary to resort to the indirect method by using the freezing point and boiling point calculations given by Jüttner.[1] These values are chosen from the work of Beckmann[2] on boiling points and Ewan[3] on freezing points. While it is a little difficult to know how to choose the best values which represent the true state of affairs, it appears that the curve for the freezing point lies above that of the vapor pressure, and the curve for the boiling point lies below. The Kirchhoff equation $L = RT^2 \frac{\partial}{\partial T}\left(\ln \frac{p}{p_0}\right)$ where L is the heat of dilution and the other symbols have their usual meanings, accounts

1 Zeit physik Chem 39 1.6 (1901)
2 ibid 4. 427 (1890)
3 ibid 37 385 (1901)

quantitatively by this device. A is defined as the mass which must be added to keep the temperature constant when one mol of solvent is added to an infinite amount of solution. Calculations based on Ewan's freezing point data and this 30° value for urea would show the heat of dilution to be greater than that observed by Ewan[1] and Stockelberg.[2]

1 loc cit
2 cit phy Chem 10 626 (1892)

Table V.

[illegible] calories per [illegible]

Molal Conc.	E (Ewan)	E (Stachelberg)	E (Gale)
1.0	-.203	-.209	-.195
2.0	-.43		-.79

[illegible] explanation for the divergence can be found in the fact that the calculated values are based on interpolated values and that the freezing point data may not be reliable starting point for the lower limit of the integral.

Because of the accuracy of the values reported it is believed that heats of dilution can be accurately determined for the higher concentrations, assuming of course, the validity of Lewis's equation.

Osmotic pressure and vapor pressure lowering.

For the thermodynamic relation between vapor pressure and osmotic pressure, the equation derived by Porter[1] is better adapted for the calculation of osmotic pressure than that of Lewis[2]. The equation of Lewis is intended to apply to ideal solutions, while Porter's equation can be applied in general. Moreover, Porter's equation is based upon the fact that the solution is under hydrostatic pressure of its own vapor which is a condition of the static method of vapor pressure determination.

Using Porter's notation where,

π_p = osmotic pressure under hydrostatic pressure p

p = hydrostatic pressure

π_1 = vapor pressure of solution when under hydrostatic pressure of its own vapor

π_o = vapor pressure of solvent when under hydrostatic pressure of its own vapor

Δ = reduction in volume when 1 gram of solvent escapes

v = specific volume of vapor

v_1 = specific volume of solvent

1 loc cit
2 J. Am. Chem. Soc. 30 667 (1908)

the relation is expressed by the equation:

$$\int_{\pi_\pi}^{p} s\,dp = \int_{\pi_\pi}^{\pi_o} v\,dp + \int_{\pi}^{p-p} u\,dp \qquad (1)$$

Assuming s and u to be independent and that the vapor obeys the gas laws, the integrated form, when simplified and terms disregarded that may be neglected, becomes:

$$P - \frac{\alpha P^2}{2} = \frac{RT}{M V_s} \ln \frac{P_o}{P} \qquad (2)$$

where P = the osmotic pressure
M = Mol. wgt. of water
α = compressibility coefficient

V_s = diminunition in volume where 1 gram of solvent is taken from an infinite amount of solution

R = gas constant

T = absolute temperature

$\ln \frac{P_o}{P}$ = values obtained from vapor pressure data - for vapor pressure solution (P) and solvent (P_o)

The V_s value may be obtained from the equation of Gouy and Chaperon[1],

$$V_s = \frac{1}{\delta}\left(1 + \frac{s}{\delta} \cdot \frac{\partial \delta}{\partial s}\right)$$

where δ = density of the solution
s = wt of solute in 1 gram of solution

1 Ann Chim Phys (6) 12 384 (1887)

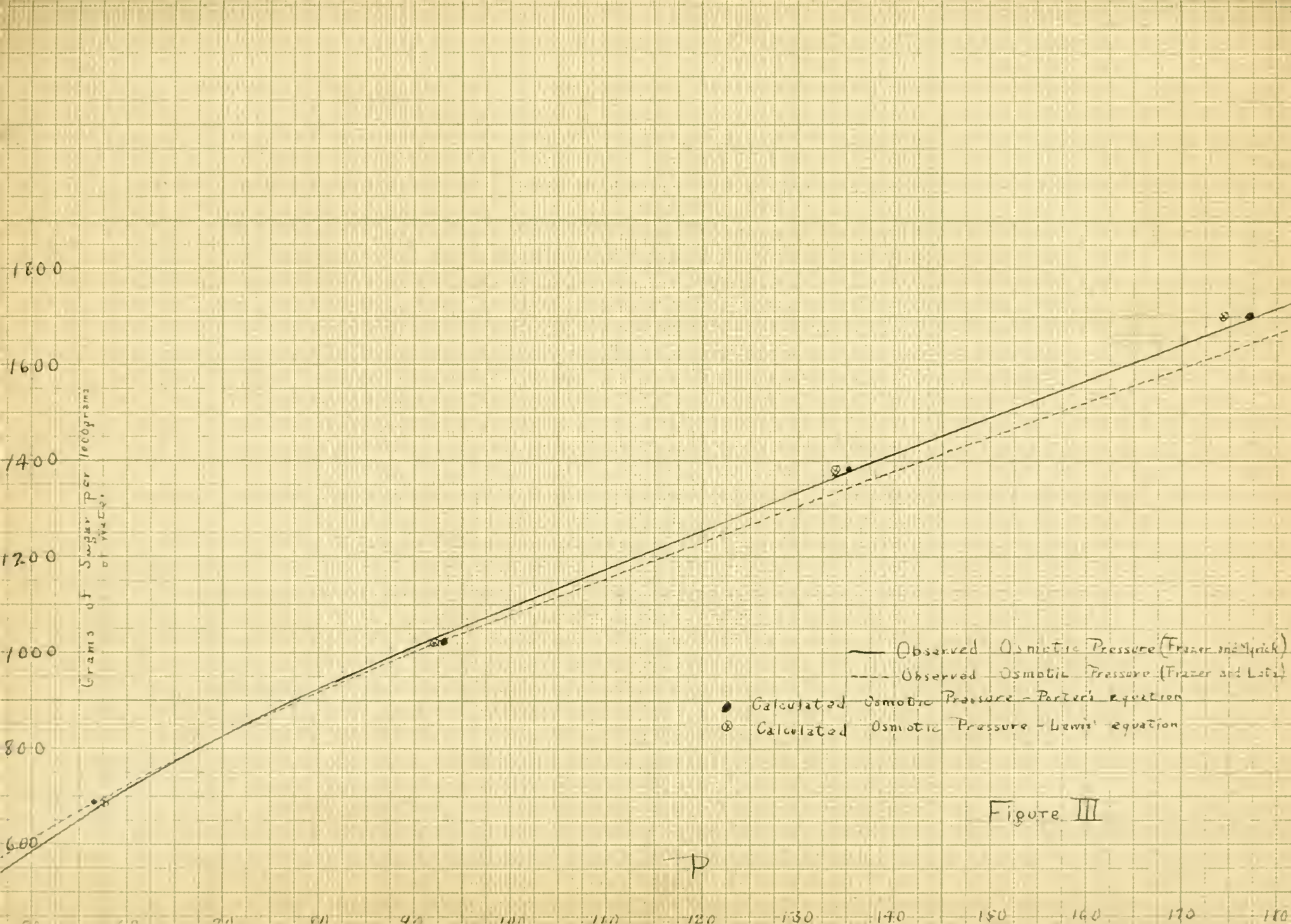

1800
1600
1400
1200
1000
800
600
Grams of Sugar per 1000grams of water.
Observed Osmotic Pressure (Frazer and Myrick)
Observed Osmotic Pressure (Frazer and Lott)
Calculated Osmotic Pressure - Porter's equation
Calculated Osmotic Pressure - Lewis' equation
P

Figure III

Calculated Osmotic Pressures of Concentrated Solutions by Porter's Equation.

In the calculation of the following values the universal gas constant Λ was used and no correction was applied to the 1M or 2M concentrations for compressibility - that data of Plato in Landolt-Börnstein Tabellen was used for the density of sugar solutions.

Table VI.

M	d	V_s	P calc	P'obs	P"obs	P"'obs
0.9937	1.1054	1.0008	25.88	26.64		
2.0162	1.1795	0.998	56.60	56.70	57.7	54.9
2.9916	1.2537	0.990	93.08	92.80	91.5	93.1
4.0363	1.3747	0.989	135.27	138.20	135.5	136.2
4.9815	1.3103	0.983	177.19	187.20	179.8	

P'obs = Lotz's[1] values corrected for temperature from 30° measurements except 1M which is value given by Morse

P"obs = Frazer and Myrick's values corrected for temperature from 30° measurements

P"'obs = Berkeley & Hartley values corrected for temperature from 0° measurements

1 Lotz Dissertation J.H.U. 1910

The agreement between the calculated and the observed is quite good except in the case of the 5M where a difference of 5.6 occurs between the calculated value and that observed by Lots with the water interferometer pressure gauge. Only in one concentration, 5M, is the calculated value higher than the observed. The correction of the observed pressures for temperatures is somewhat doubtful because the temperature coefficient of osmotic pressures at these concentrations is not known. The agreement between Frazer and Myrick's values and Berkeley and Hartley's 0° values when corrected by assuming that the solutions obey the gas law, is good, considering the range of temperature and for this reason the same method of correction of observed values was used in table VI. If heats of dilution data were available at these temperatures and concentrations perhaps that method of correction would bring the calculated and observed values nearer together. In support of this supposition take the case of the 2M solution where Lewis's[1] data can be used. The application of the Helmholtz equation according to Lewis[2] corrects the observed value so that it nearly checks the calculated value, thus:

1 loc cit
2 loc cit

$$P - \varphi = T \frac{dp}{dt}$$

φ = heat of dilution .4c calories according to Lewis

.43 c.l ≒ 13 cc atmospheres

Observed value of P at 30° according to Lotz

$$\frac{53 - 13}{295} = .13 \text{ atmospheres per degree}$$

$.13 \times 10 = 1.3$

$53 - 1.3 = 50.7$ atmospheres pressure at 20°

(50.5 calculated from vapor pressure)

Osmotic Pressures of Concentrated Solutions Calculated by Lewis' Equation.

The equation of Lewis is given as follows:

$$\Pi - \tfrac{1}{2}\alpha\Pi^2 = \frac{RT}{NV_0} \ln \frac{P_0}{P} \qquad (5)$$

Where α = compressibility

N = [illegible]

Π = osmotic pressure

V_0 = molecular volume of the solvent and the other symbols have their usual meaning.

The values calculated from this equation compare with those calculated by Morse's equation are set down in Table VII. It is evident from an examination of the table and the curve Fig. 3, that the values of equation (5) are higher

at the low concentrations [illegible] lower at the high concentrations than those of equation (3), in other words, the curves intersect at about .01 concentration.

Table VII.

Conc M	Calculated by Equation 3	Calculated by Equation 4
1	25.31	25.33
2	37.60	37.60
3	92.16	92.06
4	153.36	153.37
5	171.89	171.19

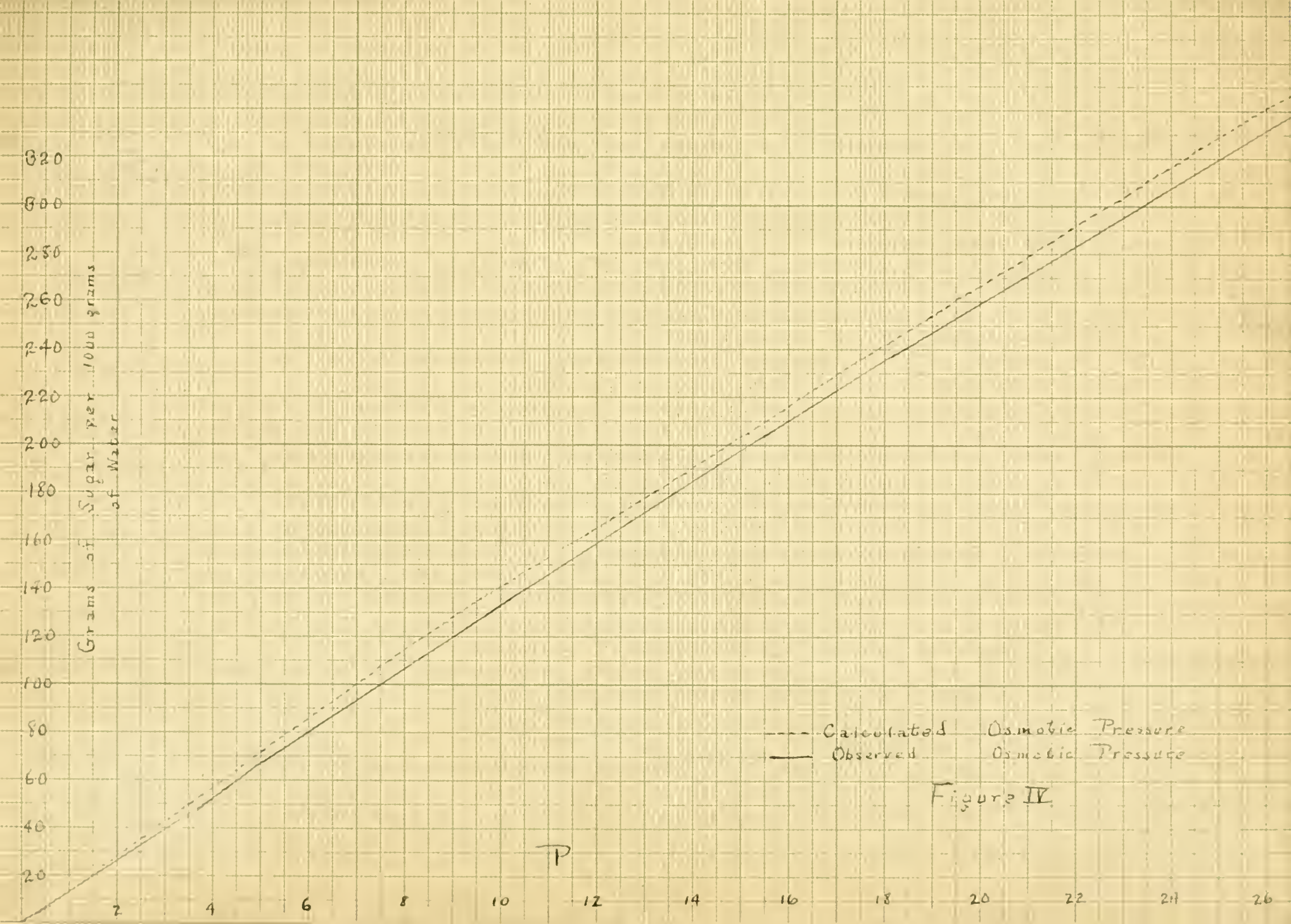

320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
Grams of Sugar per 1000 grams of Water
2
4
6
8
10
12
14
16
18
20
22
24
26
P
---- Calculated Osmotic Pressure
—— Observed Osmotic Pressure

Figure IV

however it is not safe to say that the manometer is the source of the divergence until further study has been made.

Both the equation of Lewis and that of Porter are based on the assumption that water vapor obeys the gas law. In view of the fact that there are known deviations from the gas law, this point is well worth considering, tho of course experimental evidence seems to show the divergences most marked at the higher pressures while this work is carried out under 17 mm of mercury pressure just where little or no abnormality should be shown. Batelli gives a variation in IV for water vapor at 21° of only 0.1% over a range of 10 millimeters pressure. In these vapor pressure measurements of sugar solutions it must be remembered that the vapor is saturated; and consequently at this slight pressure of 17 mm. since the experimental error in the measurement of IV of the saturated vapor is quite as reliable as that of the high ones observed, the error must be magnified in the case of saturated vapor; and thus the facts are difficult to explain one way or the other. Further study of the deviations of water vapor from the gas law at low pressures may reveal facts that will account for the difference noted above.

Table VIII.

Comparison of Measurements of Osmotic Pressures of Dilute Solutions of Mannite and Sugar by Direct and Indirect Methods.

Molar	Mannite		Sugar	
Conc	obs	calc	obs	calc
.1		2.527	2.50	2.57
.2	4.86	5.08	5.06	5.70
.4	9.59	9.89	10.13	9.68
.6	14.40	14.84	15.39	15.15
.7		16.53	15.15	17.61
1.0	24.12	25.75	25.64	25.91

Table IX.

Summary of Calculated and Observed Osmotic Pressures

g. Sugar per 1000 g. of water Morse, Myric & Frazer Lots	g. Sugar per 1000 g. of water Vapor pressure measurements	Observed by Morse & co-workers	Observed by Frazer & Myrick	Observed by Frazer Lots	Calculated by Lewis' equation	Calculated by Porter's equation
38.01	38.39	3.59			3.37	
57.33	58.13	5.06			4.70	
135.64	137.17	10.13			9.63	
203.46	206.37	15.55			15.15	
237.37	237.69	18.13			17.61	
339.1	339.54	26.64			26.01	25.36
634.4	639.54		57.7*	58.7*	57.60	56.5
1023.6	1038.13		91.5**	92.8**	93.19	93.05
1366.5	1389.39		133.5**	136.2**	135.86	135.37
1711.0	1703.67		179.8**	187.2**	174.39	177.19

* Corrected for temperature from 30° measurements by heat of dilution

** Corrected for temperature from 30° measurements by gas law

SUMMARY.

1. The vapor pressures of aqueous sugar solutions over the range of solubility at 20° have been measured.

2. The deviations of sugar solutions from Raoult's law have been recorded and discussed.

3. It has been shown that von Babo's law does not hold for sugar solutions.

4. Osmotic pressures have been calculated both for concentrated and dilute solutions by the equations of Lewis and Porter and compared with the observed values at this temperature.

BIOGRAPHY.

Hugh Klemme Parker was born in Iowa, April 11, 1894. He received his early education in the public schools of Fayette, Iowa. He was graduated from Upper Iowa University with a Bachelor of Arts degree in 1916. After teaching the scholastic year 1916-1917 in West Union Iowa High School, he entered the University of Chicago to begin graduate work. During the war he served in the Chemical Warfare Service. After his discharge from the army, he was Carnegie research assistant to Prof. Fraser of Johns Hopkins University. He entered Johns Hopkins University as a graduate student in chemistry, January 1, 1920. Physical Chemistry and Mathematics were his subordinate subjects. During the years 1921-1922 and 1922-1923 he was appointed University Scholar.